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Volatile Organic Molecules Sorption onto Carbon Nanotubes: Experiment and Molecular Modeling.

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Abstract

Two organic compounds (naphthalene and formaldehyde) were investigated for their sorption properties on to multiwall carbon nanotubes in original state and purified using acid treatment. Nice enhancement of sorptive ability was observed after nanotube purification. Smaller organic molecule was adsorbed in higher weight percentage (reaching 30 wt.%) than naphthalene (approx.13 wt.%). Molecular modeling confirmed adsorption centers of organics on carbon nanotubes being located on the outside area or close to center of nanotube, then having the lowest energy of adsorption.

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1. Introduction

A carbon nanotube (CNT) consists of one or more graphene sheets rolled into a hollow cylinder. Typical lengths and internal diameters range from 1 to 100 μm and from 1 to 25 nm, respectively. The unique combination of physical and chemical properties attributed to CNTs has made them one of the most widely utilized classes of

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engineered nanomaterials. CNTs are developed as sensors, imaging agents in gene therapy, vehicles for targeted drug delivery, nanocomposite reinforcement, hydrogen storage devices, and catalyst supports (Rümmeli 2011, Bachmatiuk 2010, Martynkova 2014, Martynkova 2007, Martynkova 2011, Matějka 2014). Multiwalled and single-walled carbon nanotubes (MWCNTs and SWCNTs) are also effective sorbents for low-molecular weight organics due to their high surface areas and hydrophobic graphene properties. Several recent studies have shown CNTs to be effective sorbents for vapor-phase toxins. CNT sorption properties in water have also begun to attract research interest with respect to the uptake of hydrophobic organic chemicals (HOCs) (Matlochová 2013). Indeed, Li 2004 reported that MWCNTs are better sorbents than carbon black for the sorption of volatile HOCs from water, and Peng 2003 and Lu 2005 observed that CNTs can effectively remove 1,2-dichlorobenzene and trihalomethanes, respectively, from water.

Two possible types of adsorption sites were proposed for carbonaceous sorbents: (i) adsorption on external surfaces, and (ii) adsorption in nanopores.

The aim of our study was to analyze adsorbed amount of organics onto MWCNT using thermal analysis. Molecular modeling was employed for prediction of adsorption centers of CNTs.

1.1. Experiment and samples

Multiwall carbon nanotubes (Nanocyl^{TM} NC 7000) were used in both form: as received and purified by acid treatment.

Purification process removes impurity and partly oxidizes the nanotube to help sorption process. At first intensive humidification in oven (heat at 5 °C/min from ambient to 250 °C and hold for 12 h) was performed. This was followed with acid treatment (2 mol. dm^{-3} HCl, stirring for 2 h), washing using distilled water till pH 7 and then centrifuged at 4000 rpm; next similarly (3 mol. dm^{-3} HNO_3 for 0.5 hour), washing using distilled water till neutral pH and then centrifuged at 4000 rpm. Last step was treatment with 20% H_2O_2 and maintained in suspension by stirring for 1 hour.

Purification morphology, observing appearance of the sample for amorphous matter, was examined using SEM. The images of original (Fig.1a) and purified samples (Fig.1b) are proving successful process of cleaning, because purified sample exposed truly fibrous character of the sample while original sample looks covered with fine amorphous particles.

Purified carbon nanotubes were exposed volatile organics for 48h in closed container at room temperature (Plachá 2008).

Two organic compounds sorption were compared: naphthalene and formaldehyde.

1.2. Analytical methods

Thermal gravimetric analysis (multi-modular thermal analyser SETSYS 1200 fy SETARAM with two measurement heads (TG-ATD 1600°C rod for the simultaneous measurement of TG and DTA curves and the head TMA – Quartz for the simultaneous measurement of thermal dilatation) was performed under 400°C in Ar inert atmosphere.

The X-ray powder diffraction (XRD) patterns were measured on X-ray diffractometer Rigaku Ultima IV (reflection mode, Bragg-Brentano arrangement, CuKα1 radiation) in ambient atmosphere under constant conditions (40 kV, 40 mA).

The micrographs of samples were performed by scanning electron microscopy (SEM) on PHILIPS XL-30.

1.3. Molecular modeling system

The computational study was made using Forcite and Adsorption locator in Biovia Materials Studio software environment. The studied structure is MWCNT containing 2 concentric nanotubes (6,6) with inner tube diameter 0.81nm and length 0.74nm, nanotubes separation is 0.3347nm. We performed a series of total energy calculations

using adsorbate locator module for naphthalene and formaldehyde. Carbon nanotubes were hydrogen-saturated before modeling. The adsorption using Forcite module with the following parameters: (energy = 1×10^{-3} kcal mol^{-1}, force = 0.01 kcal.mol^{-1}Å^{-1}, and displacement = 15×10^{-3} Å). The geometry optimization process is carried out using an iterative process, in which the atomic coordinates are adjusted until the total energy of a structure is minimized.

2. Results

2.1. Results of experimental part

The samples of both original and purified CNT were exposed for vapor of organics in closed container. The weight gain of both organics is denoted in Table 1. The highest weight difference was exhibited by sorption of formaldehyde onto purified carbonanotubes.

Table 1. Sorption differences based on thermal gravimetry results.

Sample	Weight difference [wt.%]	Sorption /CNT [mg/g]	Sorption/ CNT [mmol/g]
CNT p naph	10.5	72.3	0.56
CNT o naph	9.4	59.6	0.46
CNT p form	29.2	258.7	8.61
CNT o form	15.8	123.7	4.11

Note: CNT-carbon nanotubes, p-purified, o- original, naph –naphthalene, form-formaldehyde

Purified nanotubes (Fig. 1b) compare to original nanotubes (Fig.1a) exhibit clean fibrous morphology and amorphous powder (this has low sorptive capacity) is not visible. The acid purification is not only dissolving small amorphous particles but also activates adsorption centers functionalizing nanotubes with oxide or other chemical groups.

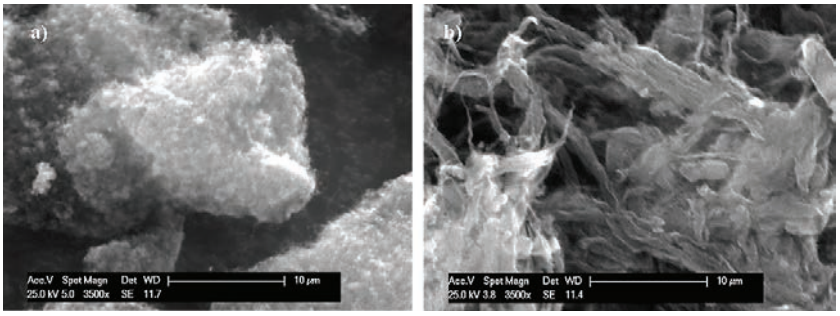


Fig. 1. SEM image of sample (a) before purification CNT- o and (b) after purification CNT-p

Thermogravimetric analysis of carbon nanotubes with absorbed organics exposed thermal behavior of material. The CNT p naph exhibits two thermal maximum on thermogravimetric curve (Fig.2), where first peak could be assigned to adsorbed naphthalene and second to reduction of activated nanotubes.

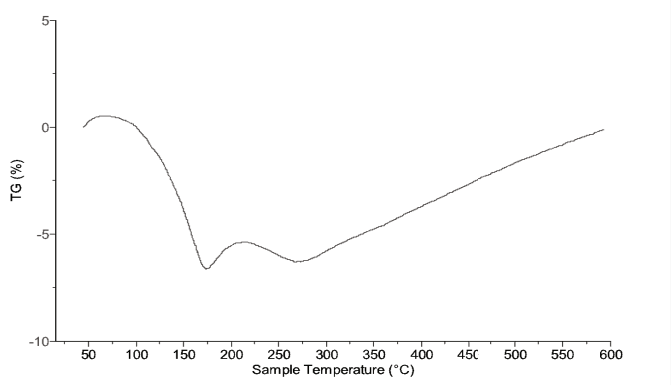
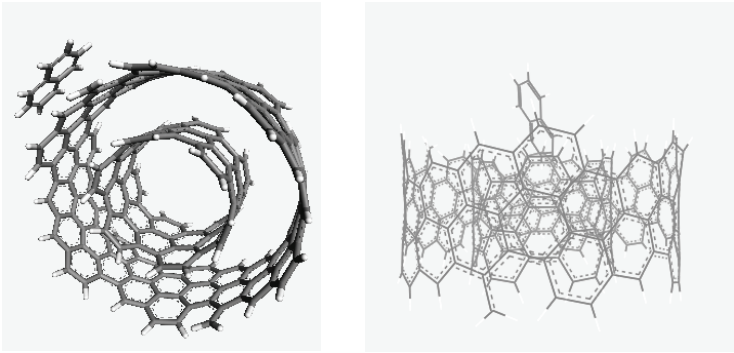


Fig. 2. Termogravimetric curve of naphthalene sample after purification CNT-p .

Molecular modeling was employed to help to predict adsorption centres of organic molecules. We studied sorption of naphthalene molecule. It was found that the lowest total energy as well as the lowest adsorption energy (Table 2) was for naphthalene molecule located at centre of nanotube (Fig.3 b).

Table 2. Molecular modeling results for naphthalene sorption

model	Total energy (kcal/mol)	Adsorp. energy (kcal/mol)	Deformation energy (kcal/mol)
Highest energy	8.62	-18.19	-3.5
Middle energy	7.79	-19.02	-3.5
Lowest energy	6.66	-20.14	-3.38



a b

Fig. 3. Molecular modeling of naphthalene adsorbed on MWCNT (a) outside located molecule – high total energy and (b) center located molecule - low total energy.

4. Conclusion

Sorption of two organic molecules – naphthalene and formaldehyde – on to multiwall carbon nanotubes were performed. The carbon nanotubes were used as received and purified using acid treatment. Experimental study of quantitative sorption was completed using thermogravimetric analysis, where weight loss was observed. Purified CNTs absorbed almost double amount of formaldehyde and slightly higher amount of naphthalene compare to original form.

Molecular modeling predicted the most advantageous position of adsorbed molecule with lowest total energy.

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